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Dynamic cyclic performance of phenol-formaldehyde resin-derived carbons for pre-combustion CO_2 capture: An experimental study

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Abstract

This study focuses on how different regeneration conditions affect the performance of two phenol-formaldehyde resin-derived activated carbons for CO_2 capture from a high pressure CO_2/H_2 gas stream, i.e., pre-combustion capture. Experimental work was conducted in a laboratory fixed-bed reactor where CO_2 adsorption was performed at high pressure (15 bar) and 45ºC, and CO_2 desorption was accomplished by reducing the pressure of the system to atmospheric (PSA process), or by coupling the pressure decrease with a rise in temperature (PTSA process). A commercial activated carbon (Calgon BPL) was used as a reference material for the separation process.

Desorption under atmospheric pressure and heating favoured the CO_2 capture rate, extract (CO_2) purity and working capacity of all the adsorbents when compared to desorption under atmospheric pressure alone. However, a higher desorption temperature in the pressure and temperature swing process (150º versus 80ºC), although it enhanced the capture rate and working capacity, it did not favour the product purity or it even penalised it. The phenol-formaldehyde resin-derived activated carbons proved to perform equal or better than the reference commercial one under almost all the different regeneration conditions studied.

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Keywords: CO_2/H_2 separation; activated carbon; phenol-formaldehyde resin; PSA; PTSA; sorbent performance

1. Introduction

In the last few years there has been strong interest in the development of adsorption technologies for capturing CO_2 from high pressure CO_2/H_2 gas streams in integrated gasification combined cycle (IGCC) processes, i.e., pre-combustion CO_2 capture. In this regard, carbon-based adsorbents have become promising materials due to their low cost, high surface area and, often, ease of regeneration and recycling.

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To date, studies have focused on how to enhance the physical interaction between the adsorbate-adsorbent and/or the adsorbent selectivity for CO_2. To this end, phenol-formaldehyde resin-derived microporous activated carbons have been previously prepared in our laboratory under different conditions (acid/basic catalysis and organic additives) to be applied as CO_2 adsorbents in a pre-combustion capture process [1]. Amongst the various synthesised activated carbons, two of them (PFCLA and PFNA) showed great potential for the above application based on: their high CO_2 equilibrium capture capacities (static) at high pressure (up to 38.5 wt% at 25 bar and room temperature) [1], and their high CO_2/H_2 selectivity and dynamic behaviour, i.e., breakthrough time, in a fixed-bed bench-scale system [2].

Solid adsorbents are usually packed as fixed beds and employed in unsteady cyclic processes composed of adsorption and regeneration steps, which result in a time-cycle. An adsorption process is controlled by the overall dynamics of the fixed-bed and it has to be designed to increase the net CO_2 working capacity of the adsorbent, to decrease the energy required for adsorbent regeneration and to increase the net recovery of the desired product gas at high purity. Because of the transient-type character of an adsorption process instead of steady-state, multiple packed-beds are often used in shifted time-cycles to achieve continuous production, and the regeneration or desorption step is often the cost-determining factor of the separation process.

An ideal solid sorbent for CO_2 capture in an IGCC process would be that one with a high CO_2 adsorption capacity coupled with a high CO_2/H_2 selectivity. However, of equal importance are the ease of regeneration and the lifetime of the adsorbent.

In this paper we debate how regeneration of two tailored-made materials is accomplished using a pressure (PSA) or a thermal and pressure swing process (PTSA) under conditions relevant to pre-combustion CO_2 capture. The process performance was evaluated in terms of CO_2 capture rate, adsorption working capacity and extract purity. Additionally, a well-known commercial activated carbon (Calgon BPL) was also tested under the same operating conditions, so it could be used as a reference. Hence, comparison between different adsorbents as well as between different regeneration strategies could be established.

2. Experimental

2.1. Materials

Two activated carbons prepared in our laboratory from Novolac, PFCLA, and Resol, PFNA, phenol–formaldehyde resins and one commercial activated carbon, Calgon BPL, have been used as the adsorbent materials in this work. The BPL carbon is a bituminous coal-based product activated at a high temperature in a steam atmosphere with a surface area of approximately 1250 m^2g^{-1} and a pore volume of 0.56 cm^3g^{-1} [3]. The PFCLA and PFNA adsorbents were prepared by carbonisation under inert atmosphere, which was followed by activation under CO_2 atmosphere up to around 40% burn-off. Details on the synthesis and characterisation of these materials have been reported and discussed in detail in an earlier paper [1]. PFCLA and PFNA activated carbons present surface areas similar to that of the BPL carbon (1211 and 1381 m^2g^{-1} respectively), high carbon contents (~ 97 wt.%) and a well-developed microporosity (total micropore volume ~ 0.5 $cm^3\ g^{-1}$).

2.2. Cyclic adsorption/desorption experiments

Experiments were conducted in a single-bed adsorption unit of $9x10^{-3}$ m diameter, where all the steps of a PSA and PTSA process can be performed. The schematic and detailed description of the system have been reported previously [4].

The full cyclic process involved three main steps: (i) pre-conditioning of the bed for 10 min, where 60 mL min^{-1} (STP) of N_2 were allowed to flow through the system so the pressure and temperature needed

for the adsorption step could be reached, (ii) feed gas switch to a $CO_2/H_2/N_2$ gas mixture (40/50/10 vol.%) to initiate the adsorption step, and (iii) depressurisation of the unit and atmospheric pressure purge with 5 mL min^{-1} (STP) of N_2 to regenerate the adsorbent. Heating was also supplied to the bed in the regeneration step during PTSA experiments. The adsorption process was carried out at 15 bar of pressure and a temperature of 45°C. This step was terminated before the CO_2 broke through the bed. A total flow rate of 100 mL min^{-1} (STP) was kept constant during the adsorption step. The regeneration step was ended before the bed was fully desorbed and different regeneration strategies were investigated: a pressure swing (PSA) process, and a pressure and temperature swing (PTSA) process conducted at two different temperatures, 80ºC (PTSA_80) and 150ºC (PTSA_150).

Measurements of the CO_2 elution profiles (tracked by a dual channel micro-gas chromatograph) during the adsorption and desorption steps enabled to calculate the CO_2 capture rate, adsorbent CO_2 working capacity and extract (CO_2) purity of a full cycle. Breakthrough experiments had been previously conducted [2, 5] to identify the appropriate step times for the cyclic experiments and obtain an estimate of the length of the mass transfer zone in the adsorbent bed. The bed parameters and duration of the adsorption and desorption steps for each adsorbent are shown in Table 1.

Table 1. Bed parameters and duration of the adsorption and desorption steps for experiments with phenol-formaldehyde resin-derived and Calgon BPL activated carbons

	PFCLA	PFNA	Calgon BPL
Height (m)	0.115	0.114	0.110
Mass of adsorbent (kg)	$3.51x10^{-3}$	$3.45x10^{-3}$	$2.97x10^{-3}$
Density (kg m^{-3})	467	464	413
Bed porosity	0.50	0.48	0.54
Total porosity	0.78	0.78	0.81
$t_{adsorption}$ (min)	11	10	5
$t_{desorption}$ (min)	11	10	5

The duration of the desorption process was set to be the same as that of the adsorption stage for all the adsorbents to simulate operation with two beds, where the feed gas passes down through one of the beds while the other is being regenerated. In each experimental run the adsorbent bed was subjected to ten consecutive adsorption-desorption cycles.

3. Results and discussion

3.1. Evaluation of regeneration strategies

The efficiency of the regeneration step, which will affect the amount of adsorbate remaining in the bed at the beginning of the next adsorption step, is dependent on the regeneration conditions used. As an example, Fig. 1 shows the CO_2 elution profiles of three experiments, carried out with the PFCLA activated carbon, which only differ on the regeneration strategy. Profiles for the two other adsorbents are qualitatively similar and therefore they are not presented here. All the tested materials were capable of adsorbing CO_2 reversibly and were found to be stable under all the conditions investigated. In a PSA process (red line) the residual CO_2 remaining in the bed after being regenerated (~ 30%) is higher than in a PTSA process, i.e., the CO_2 was not desorbed from the bed so effectively; likewise, the higher the heating temperature is in the regeneration process, the lower the residual CO_2 concentration is in the bed at the beginning of next adsorption step, going down from ~19% to ~7% when the temperature increases from 80 to 150ºC (green and blue lines, respectively).

In this work, the efficiency of the separation process was measured by three parameters: 1) CO_2 capture rate, which is the percentage of the total mass of CO_2 adsorbed in the adsorption step that is recovered in the desorption step; (2) adsorption working capacity, which is the CO_2 loading difference between the spent sorbent and regenerated sorbent and (3) product purity, which was calculated as the measured time-averaged concentrations of CO_2 at the outlet of the system in the desorption step.

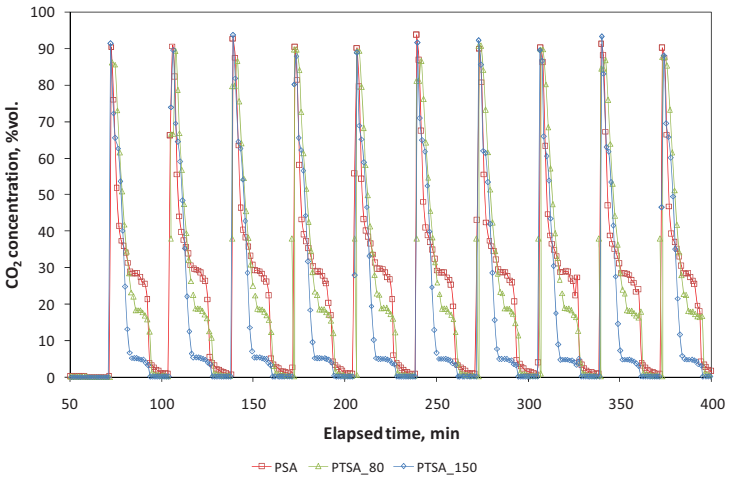

Figure 1. CO_2 elution profiles of experiments with sample PFCLA conducted under different regeneration conditions.

The influence of the regeneration conditions on the process parameters mentioned above is shown in Fig. 2 (left) for each tested adsorbent. The adsorption working capacity will influence the required sorbent inventory of the process and hence equipment size. A high working capacity is beneficial if smaller adsorption columns are targeted for the separation, so the capital and operating costs would decrease. For all the adsorbents, if heating is additionally utilised for the regeneration, the adsorption working capacity and CO_2 capture rate increase when compared to a PSA process alone. Heating has already proved to be very efficient for desorbing carbon dioxide [6-10]. In this study, a PTSA process at 150ºC led to an increase of six-eight points in percentage of capture rate when compared with regeneration without any heating, i.e., PSA. Likewise, the adsorption working capacity increased up to 5.57, 5.16 and 3.01 mmol CO_2/g ads (a 5.3, 5.2 and 8.8% increment with respect to PSA experiments) for activated carbons PFCLA, PFNA and Calgon BPL, respectively. On the downside, for a given separation, the energy requirement is usually proportional to the recovery [11], so it is important to bear in mind that if a PTSA process is utilised for regeneration as opposed to a PSA one, then the energy consumption will be impacted as well.

Regarding the purity of the CO_2 product stream, it reaches a maximum of 91.4 and 91.5% for the PFCLA and PFNA samples, respectively, when regeneration is accomplished at atmospheric pressure and a temperature of 80ºC, to slightly decrease down to 89.6 and 90.7 % CO_2 when the temperature is raised up to 150ºC. Thus, a PTSA process at relatively low temperature enhances the CO_2 purity versus a PSA process; however, the purity does not increase further with higher desorption temperatures. This effect of the desorption temperature on the CO_2 purity has been already reported in previous studies, where increasing temperatures in a PTSA process rendered a less pure CO_2 product [12]. For the Calgon BPL carbon, a pressure and temperature swing favoured the extract purity versus a pressure swing alone; however, the different temperature in the PTSA process did not penalise the CO_2 purity, which reached a

plateau at 91.2% for both desorption at 80 and 150ºC. Consequently, if the CO_2 capture rate and adsorption working capacity obtained with regeneration at 80ºC are proved to be good enough for the targeted separation process, a further increase in temperature up to 150ºC would not be worthy when considering the extra energy consumption implied in the process.

3.2. Adsorbents performance under different regeneration conditions

For a detailed comparison of adsorbents performance, Fig. 2 (right) shows the values of the different studied process parameters for each activated carbon under different regeneration conditions.

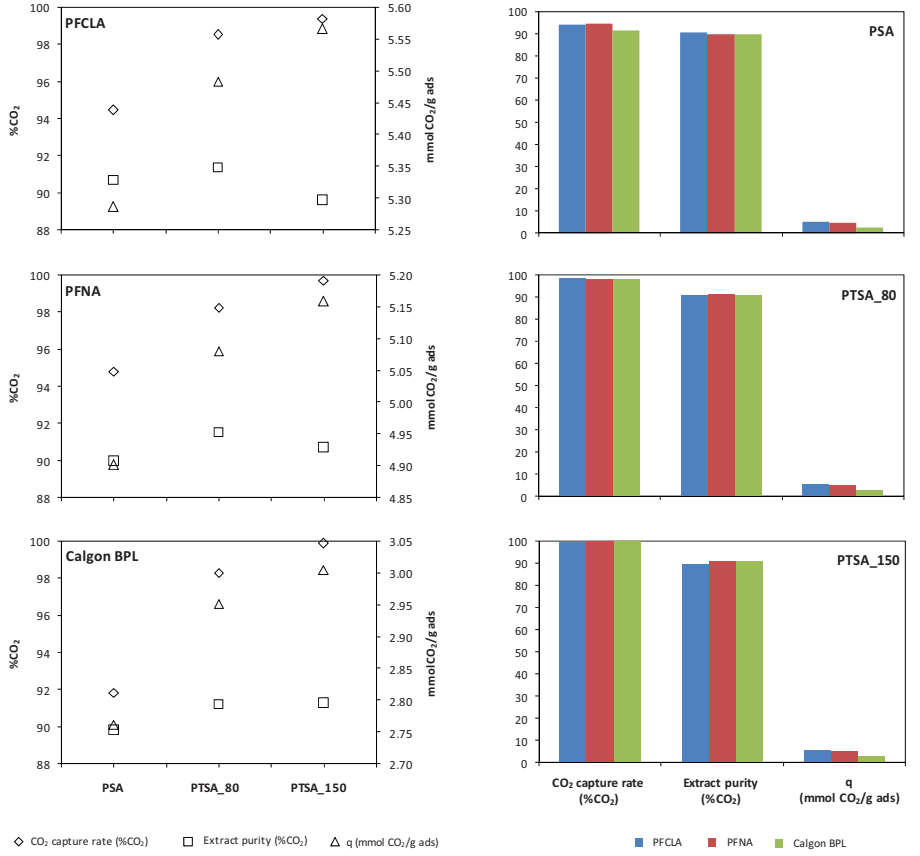

Figure 2. Comparison of regeneration strategies for each adsorbent material (left) and adsorbents performance under different regeneration conditions (right).

The phenol-formaldehyde resin-derived activated carbons performed better or equal than the reference commercial activated carbon under all the different regeneration conditions. Differences become more relevant when the CO_2 is desorbed from the bed with a pressure swing strategy alone, i.e., in a PSA

operation, than in the other two cases. Only when CO_2 is desorbed from the bed at atmospheric pressure and 150ºC, the PFCLA carbon performed worse than the commercial one in terms of CO_2 capture rate and extract purity.

4. Conclusions

This study experimentally investigated the performance of three (two tailored-made and one commercial one) activated carbons in cyclic dynamic experiments for the recovery of CO_2 from syngas-shifted gas streams in an IGCC coal based-power plant. The merit of the adsorbent materials was judged by subjecting them to the same PSA and PTSA cycles and by comparing relevant process parameters (CO_2 capture rate, product purity and adsorption working capacity).

All the materials were capable of adsorbing CO_2 reversibly and were found to be stable under all the conditions used in this study. Adsorbent regeneration with heating, i.e., a PTSA process, proved to be more effective than regeneration at atmospheric pressure alone, i.e., a PSA process, since the values of CO_2 capture rate and working capacity were enhanced for all the adsorbents. Higher temperatures in the PTSA process, however, did not favour the product purity and for the PFCLA and PFNA activated carbons, it even penalised it.

The phenol-formaldehyde resin-derived activated carbons performed equal or better than the reference commercial one under all the different regeneration conditions studied (except for the PFCLA carbon in experiments with regeneration at atmospheric pressure and 150ºC).

It can be then concluded that the tailored-made activated carbons studied here have a great potential to be applied in a CO_2 pre-combustion capture process. Currently, further research is being conducted in order to optimise the efficiency of the PSA system, so the energy input can be reduced to render the process economically viable and competitive.

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